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Highlights

- Likely huge reservoir of BFRs associated with waste soft furnishings
- Little is known about mechanisms via which BFRs migrate from such waste materials
- Few studies exist of BFR emissions from regulated waste treatment activities
- BFR emissions from waste soft furnishings a potential serious environmental concern

EXTENT AND MECHANISMS OF BROMINATED FLAME RETARDANT EMISSIONS FROM WASTE SOFT FURNISHINGS AND FABRICS

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Abstract

Use of BFRs in soft furnishings has occurred for over thirty years with the phase out of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) only relatively recently begun. As products treated with BFRs reach the end of their lifecycle they enter the waste stream, thereby constituting an important and increasing reservoir of these chemicals. This review highlights the dearth of data on the extent and potential mechanisms of BFR emissions from waste soft furnishings. However, insights into what may occur are provided by scrutiny of the larger (though still incomplete) database related to BFR emissions from electronic waste (e-waste). In many countries, municipal landfills have historically been the primary disposal method of waste consumer products and therefore represent a substantial reservoir of BFRs. Published data for BFR emissions to both air and water from landfill and other waste disposal routes are collated, presented and reviewed. Reported concentrations of PBDEs in landfill leachate range considerably from <1 ng L^{-1} to 133,000 ng ΣPBDE L^{-1}. As well as direct migration of BFRs from waste materials; there is evidence that some higher brominated FRs are able to undergo degradation and debromination during waste treatment, that in some instances may lead to the formation of more toxic and bioavailable compounds. We propose that waste soft furnishings be treated with the same concern as e-waste, given its potential as a reservoir and source of environmental contamination with BFRs.

Keywords

Tetrabromobisphenol-A

Hexabromocyclododecane

Polybrominated diphenyl ethers

Waste soft furnishings

Migration

Landfill

1. Introduction

Brominated flame retardants (BFRs) are a group of synthetic chemical additives that over the last 30 years or so, have been applied to a wide range of consumer products such as: building materials, electronics and electrical goods, textiles and furnishings, to meet and comply with fire safety standards. Currently there are more than 75 different commercially-recognised BFRs. Moreover, BFRs have historically been the most widely used flame retardants (FRs) due to their low cost and high efficacy (Covaci et al., 2008). The five classes of BFR that have found most widespread use are tetrabromobisphenol-A (TBBP-A), hexabromocyclododecane (HBCD), and three technical mixtures of polybrominated diphenyl ethers (PBDEs): Penta-BDE, Octa-BDE, and Deca-BDE (Leonards et al., 2008). In an environmental context, BFRs are highly resistant to degradation whether through chemical, biological, or photolytic processes and are therefore capable of long range transport, bioaccumulation in human and animal tissues and potential trophic magnification. As a result, widespread contamination of air, water, soil, sediment, and terrestrial and marine biota by BFRs has been widely documented (Law et al., 2006; Law, 2010; Harrad et al., 2009b; Harrad et al., 2010a; Muir and de Wit, 2010).

These considerations are exacerbated by evidence of the toxicity of some BFRs. HBCD has been identified as an endocrine disruptor that induces enzymes and alters thyroid homeostasis with potential to cause adverse effects in humans at relatively low exposure levels (Darnerud, 2003, 2008; Yamada-Okabe et al., 2005; van der Ven et al., 2006, 2009). With respect to PBDEs, acute toxicity studies have suggested that they can be hepatotoxic at relatively high doses (Zhou et al., 2002; Bruchajzer et al., 2011). Moreover, several studies have indicated that Penta- and Octa-BDE mixtures, as well as several of the major individual congeners present in wildlife and people, can alter liver enzymes, disrupt thyroid homeostasis, and are associated with early onset of puberty, reduced fertility, and impaired neurological development (Viberg et al., 2007). This latter effect is illustrated by a cohort study of 329 pregnancies in New York City, in which prenatal PBDE exposure (as indicated by cord blood PBDE levels) was associated with lower mental and physical development test scores for children aged 1, 4, and 6 years (Herbstman et al., 2010). In general, the lower brominated congeners are more

acutely toxic than the higher ones (Darnerud, 2003). While BDE-209 is relatively less persistent and bioaccumulative than the lower brominated congeners, it has nonetheless been shown to increase the incidence of adenomas and carcinomas during chronic toxicity studies in rodents (Kelly et al., 2008; NTP, 1986, Tomy et al., 2008; Wu et al., 2009). Moreover, work by Johansson et al., (2008) suggests that decabromodiphenyl ether (BDE-209) can be as potent as the lower brominated PBDEs in causing developmental neurotoxic defects. In contrast, TBBP-A is relatively less persistent and bioaccumulative than most other BFRs (Domínguez et al., 2011). Furthermore, it is not acutely toxic (WHO, 1995) and the toxicity and teratogenicity of TBBP-A appeared low in experimental *in vivo* studies (Darnerud, 2003). However, TBBP-A is a potential endocrine disruptor, acting as a thyroid hormone and oestrogen agonist (Meerts et al., 2000; Kitamura et al., 2002, 2005), and additionally has been reported to be immunotoxic as a result of its *in vitro* inhibition of a key T-cell receptor (Mariussen and Fonnum, 2003).

Human exposure to BFRs occurs predominantly via indoor dust and food ingestion (mainly oily fish, meat, dairy products, and the neonatal sources of human milk and placental transfer), with a minor contribution from inhalation (Abdallah and Harrad, 2009; Covaci et al., 2009; Frederiksen et al., 2009). Concentrations of BFRs are higher in indoor air than outdoor air; this is likely due to the usage and slow release of BFRs from consumer products and building materials (Sjödin et al., 2001; Takigami et al., 2007; Abdallah et al., 2008; Toms et al., 2011).

These concerns about their adverse environmental impacts have meant that production of the Penta- and Octa-BDE commercial mixtures ceased in the EU and North America in 2004, and their use in all applications in 2006. Likewise, Deca-BDE was restricted severely in the EU in 2008, with US manufacturers voluntarily committing to phase it out from most uses in the USA by the end of 2012, and to end all uses by 31 December 2013. As a further reflection of concern about their use, the Penta- and Octa-BDE commercial mixtures (Tetra-, Penta-, Hexa- and Hepta-BDEs) and HBCD are listed as persistent organic pollutants (POPs) under the UNEP Stockholm Convention, while Deca-BDE is under active consideration for listing.

1.1 BFR production and applications

In 2005, the total annual usage of BFRs was estimated to be about 311,000 tonnes, 130,000 tonnes of which was TBBP-A (Harju et al., 2008). HBCD annual production was estimated at up to 28,000 tonnes (9,000 to 15,000 tonnes in China, 13,426 tonnes in Europe and the US) (UNEP, 2011). Total historic production of PBDEs (including Deca-BDE) has been estimated to amount to 1.3 million to 1.5 million tonnes between 1970 to 2005 (UNEP, 2010a).

There are essentially two modes via which BFRs are incorporated into polymers. One is referred to as additive; in this instance the BFR is added to the molten polymer. This "additive" mode means that the BFR is not tightly bound to the polymer and therefore its migration to the environment is relatively facile. The alternative approach is where the BFR is covalently-bound to the polymer via reaction. Release to the environment of BFRs incorporated via this "reactive" process is comparatively restricted (Law, 2010). A caveat however, is that during the process of incorporation into the treated product, a proportion of the reactive BFR used may not polymerise, and this residual fraction has potential to be released to the environment (de Wit, 2002). TBBP-A is primarily used as a reactive FR in epoxy, polycarbonate and phenolic resins in printed circuit boards (58%), but has also been used as an additive BFR in the manufacture of acrylonitrile-butadiene-styrene (ABS) resins (18%), and was "possibly" used as an additive in high impact polystyrene (HIPS) (BSEF, 2009; EFRA, 2007). Concentrations of TBBP-A commonly found in these applications are between 10% and 20% by weight, depending on the polymer (Covaci et al., 2009). Moreover, during the 1990s, TBBP-A was increasingly used as a replacement for Octa-BDE in ABS polymers (Watson et al., 2010).

The available data indicates that in general PBDEs (all congeners) were added at concentrations between ~3-30% by weight (WHO, 1994). The exact concentration applied was determined by several considerations such as the degree of flame retardancy required, the efficacy of the FR selected, whether it is applied in

conjunction with a synergist (e.g. antimony oxide), physical attributes of the end product (e.g. colour, density, stability, etc.), and its specific application (European Chemicals Bureau, 2000).

In Europe approximately 95% of Penta-BDE was used in flexible polyurethane foam (PUF), mainly used for furniture upholstery and automotive applications (European Chemicals Bureau, 2000). The United Nations Environment Programme (UNEP) initially reported treated PUF to usually contain 10-18% by weight of Penta-BDE, however they have subsequently revised these estimates to be around 3-5% by weight for upholstery, cushions, mattresses, and carpet padding (UNEP, 2006a; UNEP 2010a). A similar concentration range of between 6-18% by weight of Penta-BDE in PUF was provided in the Plastics Additives Handbook (Zweifel, 2001; cited in EC, 2011). The remaining minor uses of Penta-BDE (totalling 5%) include: textiles, printed circuit boards, insulation foam, cable sheets, conveyor belts, lacquers, and possibly drilling oils (UNEP, 2007). UNEP reported that the approximate distribution of global Penta-BDE use was 60% in furniture and 36% in transport, with the remaining 4% deployed in other articles (UNEP, 2010b).

Historically, around 95% of Octa-BDE supplied in the EU was used in ABS (globally ~70%), to which it was typically added at concentrations between 10-18% by weight (EC, 2011). The main uses for BFR-treated ABS were predominantly in housings of electrical and electronic Equipment (EEE), particularly for cathode ray tube (CRT) housings (e.g. PC monitors and TVs), and office equipment (e.g. copying machines and business printers). The remaining ~5% of minor uses were in HIPS, polybutylene terephthalate (PBT), and polyamide polymers, with typical concentrations between 12-15% by weight. Other possible uses were in: nylon, low density polyethylene, polycarbonate, phenolformaldehyde resins, and unsaturated polyesters, as well as in adhesives and coatings (UNEP, 2010a; 2010b).

Widely used due to its relatively low cost, Deca-BDE was employed as a back coating on a wide range of fabrics, including: nylon, polypropylene, acrylics, and many other blends such as polyester-cotton (Weil and Levchik, 2008). Typically, Deca-BDE was

added at about 10-25% by weight in a 2:1 weight ratio with antimony oxide (Weil and Levchik, 2008). Important applications were in: automotive upholstery, draperies for hotels and public buildings, and institutional (e.g. office) upholstered furniture (Weil and Levchik, 2008).

The principal use of HBCD (90%) is in the building industry, typically added at <3% by weight into extruded or expanded polystyrene foam in rigid insulation panels/boards (EC, 2011; Marvin et al., 2011), with a further ~2% deployed in HIPS used for electric and electronic equipment (distribution boxes for electrical lines and electrical housings) (EC, 2011). However, HBCD is also used as a textile coating agent in polymer dispersions applied to cotton or cotton/synthetic blends for upholstery fabrics, e.g. residential and commercial upholstered furniture and transportation seating, bed mattress ticking, draperies and wall coverings, interior textiles, e.g. roller blinds, and vehicle interior textiles. HBCD can also be used in thermosol treatment of polyester, polypropylene and nylon fabrics, where it is applied as an aqueous suspension or emulsion at a loading of 8-11% by weight (Weil and Levchik, 2008).

The above underlines the extensive global use of BFRs in a wide range of applications, and demonstrates that while deployment in electronic and electrical equipment (EEE) is substantial; use in soft furnishings is extensive also. While attention to date has understandably focused largely on emissions during the production and use phases of the product life cycle; the fact that a considerable proportion of the BFR inventory has either entered or is moving towards the end-of-life phase, means that attention is increasingly turning towards the environmental implications of BFRs associated with waste materials. In particular, considerable interest has been aroused in potential BFR contamination from landfilled waste. At the beginning of the 21st century, the majority of BFR-containing consumer products ended up as untreated waste in landfill, with Alcock et al. (2003) estimating that >80% of total BFR-containing waste was landfilled in the UK and North America. The lifespans of the principal products containing TBBP-A, PBDEs, and HBCD are estimated to be ~10 years for soft furnishings and furniture, ~12 years for cars, but <10 years for EEE; with lifespans of EEE decreasing as the rate of obsolescence for these products hastens. Consequently, as European use of these BFRs

in new goods peaked in the mid 1990s and has decreased substantially to zero since; many articles containing PBDEs (EEE in particular) have most likely already become waste and been treated by the existing waste management infrastructure. Essentially therefore, most products containing PBDEs in Europe have probably been landfilled already. This therefore represents a significant reservoir in landfilled waste. However, studies of emissions of BFRs from such waste are few.

1.2 BFRs in waste soft furnishings and furniture

In the UK alone, WRAP (2012) estimated that around 670,000 tonnes of furniture and 310,000 tonnes of textiles are disposed of by householders annually. This estimate was extrapolated from data collected across the UK during 2010/11. Considering that these products were often treated with BFRs at percent levels by weight (UNEP, 2006a; UNEP 2010a; Weil and Levchik, 2008), it is apparent that they constitute a significant potential source of BFRs to the environment. Despite this, very little research has been undertaken that examines end of life management of BFRs associated with waste soft furnishings and furniture.

1.3 Overview of UK landfills as a case study for the developed world

Landfill has been the dominant waste management option in the UK for many years. Introduction of the European Directive 1999/31/EC on the Landfill of Waste (Landfill Directive) aimed to reduce the dependence on landfill as a disposal option. Its intention was to lessen the environmental impact of landfills and diminish the overall risk to human health. Before 2004, the UK disposed of both hazardous and non-hazardous wastes together at the same landfill, a practice known as co-disposal. Since July 2004, co-disposal is no longer practised and instead, landfills are divided into three distinct classes in which only specific waste types may be disposed of: landfills for hazardous waste, landfills for non-hazardous waste, and landfills for inert waste (Council of the European Union, 1999).

From October 2007, it became a requirement that waste sent to landfill be pre-treated. This change aims to increase waste recycling and recovery and reduce pollutant emissions from landfills (Environment Agency, 2011). The process of

treatment must change the characteristics of the waste, and it must do so in order to substantially:

(a) Reduce its volume; or

(b) Reduce its hazardous nature; or

(c) Facilitate its handling; or

(d) Enhance its recovery potential.

The treatment of waste can be achieved by many methods depending on the aim of the treatment. These may include: manual sorting to change waste characteristics, physical (mechanical) treatment (crushing, grading, magnetic separation, eddy current separation, ballistic separation, trommeling (a revolving cylindrical sieve used for screening or sizing waste), and sorting, etc.), thermal treatment, and chemical or biological processes (anaerobic/aerobic digestion, biological stabilization of 'black bin' residues) (Environment Agency, 2011; Council of the European Union, 1999).

The Landfill Directive also places more stringent engineering and operation conditions on landfill operators. During the active phase and following closure of a site, a monitoring regime must be implemented to ensure groundwater quality is not compromised. Groundwater protection measures require that there is no discharge of a prescribed range of hazardous substances (including organohalogen compounds such as pesticides and herbicides, but not BFRs) to groundwater and that formal compliance points below a landfill have been established, where both leachate and groundwater composition must be monitored.

It is now mandatory for new landfills in developed nations to be engineered using a liner membrane barrier to separate the landfilled waste from the underlying ground. This membrane retards migration of leachate into surrounding groundwater. It generally comprises a layer of compacted clay with a minimum required thickness and a maximum allowable hydraulic conductivity, overlaid by a high-density polyethylene (HDPE) geomembrane. By doing so, the intention is that in the event of a hole developing, the impact of any leak will be minimised as there will also be clay below the HDPE as a further line of defence. All membranes are slightly porous and over time low volumes of leachate cross the membrane. The landfill membranes are designed

such that at these low volumes the leachate should never have a measurable adverse impact on the quality of the receiving groundwater.

However, the US EPA (1988) has voiced concerns that “once the unit is closed, the bottom layer of the landfill will deteriorate over time and, consequently, will not prevent leachate transport out of the unit.” Therefore it can be said that modern landfill designs delay, but do not wholly prevent ground and surface water pollution. Laid on top of the membrane is a series of leachate collection pipes to transport the leachate to a collection or treatment location. The failure or abandonment of the leachate collection system poses a more significant risk to groundwater. As landfills age they are prone to suffer large internal movements as waste decomposes unevenly. Consequently leachate collection systems are susceptible to internal failure and pipes can buckle and distort. Such failure causes leachate levels to slowly build within the landfill, and given time they may even rise sufficiently high to spill over the top of the containing membrane at uncapped sites. A positive feedback mechanism can then occur, in which further active decomposition and leachate generation can be triggered as leachate levels rise and rehydrate previously dried out waste masses. One of the many problems leachate collection systems can face, is clogging of the conduit pipes with mud or silt. The conditions in leachate collection systems are ideal for micro-organisms to multiply and this growth can exacerbate the clogging problem. Another mechanism via which clogging can occur is by chemical reactions within the leachate which in turn generates solid residues. Furthermore, the pipe walls may be weakened by the chemical composition of the leachate and cause them to fail. Simulations by Danon-Schaffer et al., (2013a) suggest that concentrations of PBDEs will continue to be significant in landfills beyond 2080, and that PBDEs contained in existing landfilled waste will persist to nearly 2070.

Within the UK, the waste electronic and electrical equipment (WEEE) Regulations came into force in July 2007. This requires collection of 65% of e-waste, and recovery of 85% of the collected material. This means that 35% of UK e-waste can still be disposed to landfill untreated, augmenting the already substantial quantity of e-waste residing in

UK landfills. However, no regulations exist that address the disposal of waste soft furnishings.

2. Mechanisms of BFR migration from goods and materials and their behaviour

The mechanisms via which BFRs transfer from waste products to the environment remain an active field of investigation. PBDEs and HBCD are used primarily as additives and therefore migrate comparatively readily from the surface of products within which they are incorporated into the environment (Deng et al., 2007). In contrast, TBBP-A is used predominantly (though not exclusively) as a reactive BFR and therefore its release from treated goods is much less pronounced than for PBDEs and HBCD. This is exemplified by the low concentrations of TBBP-A reported in indoor air, dust and food (Covaci et al., 2009). In addition to migration from waste materials following disposal to landfill, evidence also exists to suggest that transport of waste materials to disposal sites and their subsequent storage before sorting or deposition may also prove to be significant emission pathways for BFRs to the environment (Julander et al., 2005; Muenhor et al., 2010). The following sections summarise current knowledge relevant to our understanding of how BFRs are emitted to the environment as a result of waste management.

2.1 Emissions to air

Emission chamber experiments conducted by Kemmlein et al., (2003) documented emissions of BFRs via volatilisation from a range of consumer products including insulating materials, assembly foam, upholstery/mattresses, and electronics equipment. An increase of temperature (from 23 to 60 °C) was found to cause a 500-fold increase in emissions of BDE-47 from printed circuit boards. This has relevance for emissions from waste, as within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat released during aerobic degradation (Kjeldsen et al., 2002; Environment Agency, 2002). Consequently, elevated volatile emissions of BFRs from active landfills are plausible. However, the study of Kemmlein et al (2003) also showed BFR emissions to vary between products, and of particular relevance to this review, emissions of HBCD and Deca-BDE from the PUF and textile components of an upholstered stool were not detected over a period of 170 days. Conversely, chamber

experiments by Wilford et al., (2003) showed that PBDEs volatilise from PUF at significant levels. Both studies showed that different PBDE congeners are released at different rates, determined by their physical properties i.e. higher emissions observed for congeners with higher vapour pressures (Table 1 - Kemmlein et al. 2003; Wilford et al., 2003).

More recently, Kajiwara and Takigami (2013) conducted emission chamber tests on three curtain textile samples. Two of the samples were treated with technical HBCD and one with technical Deca-BDE. Tests were conducted over a range of temperatures (20, 40, 60, and 80 °C) for 120 hours. Both HBCD and BDE-209 (the least volatile PBDE) were found to volatilise at 20 °C indicating that they are emitted from textiles even at room temperature. At temperatures of 80 °C, HBCD emission rates were increased twenty-fold compared to the rates at 60 °C, with those of Deca-BDE at 80 ˚C six times greater than at 60 °C. There were no clear differences between the emission rates at 20, 40, and 60 °C for both BFRs.

The few studies that have reported concentrations of BFRs in air at or near landfill sites are summarised in Table 2. Weinberg et al., (2011) reported particulate phase concentrations of BDE-183 at both active and closed landfill sites in Germany to fall between 0.001 to 0.011 ng m^{-3} and 0.001 to 0.003 ng m^{-3} respectively. The authors suggested that the significantly higher ($p < 0.05$) detection of BDE-183 at the active landfill site compared to the closed site, indicates that BDE-183 might be emitted from waste disposed at the active landfill. However, the study failed to detect PBDEs in the vapour phase at either site, despite other European and UK background studies reporting low concentrations in air, typically sub- to a few pg m^{-3} (Gioia et al., 2006; Lee et al., 2004). In Canada, St-Amand et al., (2008) reported concentrations of PBDEs collected at a sanitary landfill near Ottawa. Vapour and particulate phase total PBDE concentrations were generally below 0.002 and 0.02 ng m^{-3} respectively and ranged from 0.00036 to 0.0069 ng m^{-3} and 0.00072 to 0.145 ng m^{-3}, respectively. These concentrations are in line with those detected at other locations not impacted directly by point sources. In contrast, Oliaei et al., (2010) reported the total ΣPBDE concentration of vapour and particulate phases combined in “ambient air of diffused

landfill gas" at a recently closed landfill in Minnesota, USA was 17.3 ng m^{-3}. BDE-47 had the highest concentration (8.23 ng m^{-3}), followed by BDE-209, -99, -28/33, and -100. BDE-209 was found predominantly in the particulate phase, while lower brominated BDEs were principally in the vapour phase. These data suggest strongly that the landfill studied was a source of PBDEs.

Given the paucity of data related to BFR concentrations in air in the vicinity of landfills; Table 2 also summarises other data that illustrate the potential for emissions of BFRs to air from waste products. In the UK, Harrad et al., (2010a) reported elevated concentrations of HBCD in outdoor air sampled within the boundaries of an e-waste treatment facility (22 ng ΣHBCDs m^{-3}). Likewise, Julander et al., (2005) detected up to 214.3 ng m^{-3} Σ_{24}PBDEs in airborne particulates sampled in the vicinity of an e-waste recycling facility in Sweden. Moreover, in addition to the data summarised in Table 2, other studies have reported elevated concentrations of PBDEs in indoor air and dust within WEEE recycling facilities (Rosenberg et al., 2011; Sjödin et al., 2001; Takigami et al., 2006).

Emissions of BFRs are also plausible as a result of combustion of waste. Rupp and Metzger (2005) qualitatively investigated the reaction of BDE-47 and BDE-153 between 250 °C and 500 °C. At such comparatively low temperatures, PBDEs are not destroyed completely and thus may potentially act as precursors for the formation of e.g. polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs). Interestingly, the same study revealed that thermal treatment of both BDE-47 and BDE-153 resulted in the formation of monochlorinated polybrominated diphenyl ethers (CPBDEs) (Rupp and Metzger, 2005).

Such combustion emissions can occur either accidentally (as in landfill fires), or intentionally via incineration of municipal solid waste (MSW). MSW is by nature a heterogeneous mix of waste that will contain varying proportions of waste furniture and fabrics. The concentration of ΣPBDEs outdoors at a MSW incineration plant in Tagish, Yukon, Canada was reported as 2 ng m^{-3} (Alaee, 2001). Agrell et al., (2004) sampled air outside a MSW incineration plant in Malmö, Sweden. They reported

concentrations of ΣPBDEs (BDE-28, -47, -66, -100, -153, -154, -183) for vapour and particulate phases combined that ranged between 0.00224 and 0.02132 ng m^{-3}; with a median value of 0.0063 ng m^{-3}. However, the authors note that the low concentrations were likely due to the sampling having taken place during cool periods (mean 8 °C, 17th October-9th November 2001 and 19th February-15th March 2002) when volatilisation from contaminated surfaces was less facile. Concentrations of ΣPBDEs and BDE-47 were significantly higher at the MSW incineration plant compared to those at an urban background site. In Japan, PBDE output from incinerator stack emissions were reported as 65,000 ng/h, equivalent to an emission factor of 100 ng PBDE emitted per g waste incinerated) (Sakai et al., 2006). Investigations by Takigami et al., (in press) into the incineration of XPS and EPS insulation foams show that HBCD is destroyed almost entirely during the combustion process and resulting emissions are negligible (destruction efficiency of 99.9999%). It appears reasonable to assume that HBCDs in treated fabrics may exhibit similar behaviour during incineration. Finally, Tu et al., (2011) reported emissions of Σ_{30}PBDEs measured in stack flue gas at two MSW incinerators in southern Taiwan. PBDE concentrations were 9.32 ng/Nm^3 and 7.62 ng/Nm^3 again equating to an emission factor of 100 ng PBDE emitted per g waste incinerated.

2.2 Leaching to groundwater

Percolation of water through almost any material will cause soluble components to be dissolved out and enter the leachate. Insoluble liquids (such as oils) and small particles in the form of suspended solids may also be present in leachate (Environment Agency, 2002). Leachate composition is primarily determined by the composition and solubility of the waste constituents. The composition of waste can be said to change over time as a landfill ages (for example due to weathering or biodegradation) and therefore the leachate composition also changes with time. This is particularly the case in landfills containing non-hazardous municipal waste. Generally, it is accepted that landfilled waste undergoes at least four phases of decomposition and therefore four stages in the generation of leachate. These are: (1) an initial aerobic phase, (2) an anaerobic acid phase, (3) an initial methanogenic phase, and (4) a stable methanogenic phase (Christensen and Kjeldsen, 1995).

1. Leachate produced in the early stages of decomposition of waste is typically generated under aerobic conditions producing a complex solution with near neutral pH. This phase generally only lasts a few days or weeks because oxygen is not replenished once the waste is covered. It is relatively unimportant in terms of leachate quality, as most leachate produced during this phase results from the release of moisture during compaction and bypassing of precipitation through the buried refuse. However, because aerobic degradation produces heat, leachate temperatures can rise, sometimes as high as 80-90 °C, and if this heat is retained it can enhance the latter stages of leachate production (Kjeldsen et al., 2002; Environment Agency, 2002). Elevated temperatures are likely to enhance potential volatilisation and also the aqueous solubility of BFRs.
2. As decomposition processes develop and oxygen sources are depleted, the waste becomes anaerobic, supporting fermentation reactions. The anaerobic phase has two main stages in leachate generation; the acidogenic stage and the acetogenic stage. The acidogenic stage proceeds efficiently over a relatively narrow pH range around neutral. During the acetogenic stage, hydrolytic, fermentative, and acetogenic bacteria dominate, resulting in an accumulation of carboxylic acids, and a pH decrease. This acidic pH leachate is chemically aggressive and increases the solubility of many compounds (Kjeldsen et al., 2002; Environment Agency, 2002).
3. After several months or years, methanogenic conditions are established as the pH of the waste becomes sufficiently neutralised to permit at least limited growth of methanogenic bacteria. The leachate becomes neutral or slightly alkaline as the pH increases and acids are consumed. The overall volume of leachate is lower but still contains significant quantities of some pollutants (e.g. ammonium).
4. As biodegradation nears completion, the pH continues to increase and aerobic conditions may return. Some organic compounds are present in the leachate, mostly recalcitrant compounds such as humic and fulvic acids (Environment Agency, 2002; Kjeldsen et al., 2002). The implication of the continued presence

of humic acids is that they enhance the leachability of BFRs from waste materials they contact.

Over time, leachate barrier systems are prone to degradation and ultimately failure. When this occurs, pollution of groundwater becomes possible. Alternatively if leachate is not removed for treatment at sufficiently high rates, seepage to both surface and groundwater may occur (Slack et al., 2007). The processes via which BFRs leach from landfilled waste are not yet understood. In order to understand these leaching mechanisms, a full knowledge of the environmental partitioning mechanism at aqueous/solid-phase interfaces is required, as well as the relevant physicochemical properties of BFRs (Choi et al., 2009).

PBDEs are hydrophobic, therefore their presence in leachate implies that other constituents present in the leachate have enhanced their leachability. When wastes come into contact with rainwater in a landfill, relatively hydrophilic BFRs such as TBBP-A are more readily dissolved in the leachate (Osako et al., 2004). However, dissolved humic matter (DHM) in the leachate interacts with hydrophobic BFRs such as the higher brominated PBDEs in the waste and can enhance their leachabilities (Osako et al., 2004).

Danon-Schaffer et al., (2013b) conducted a series of leaching experiments contacting e-waste with distilled water and leachate from a major urban landfill in end-over-end contactors at a rotational speed of 8 revolutions per minute. The authors found greater transfer of PBDEs to the aqueous phase at lower pH levels (4 and 5). The authors hypothesised that changes in pH affect the solubility and mechanical properties of the plastic, influencing the dislodgement of fine particles from the polymer. Compared to when e-waste was contacted with leachate, contacting e-waste with distilled water resulted in a lower transfer of PBDE concentrations to the aqueous phase. The duration of contact time (1 to 168 h) appeared to exert little influence on the transfer of PBDEs to the distilled water. Likewise, when leachate was used (over experimental durations of 1 to 654 h), relatively little PBDE was transferred to the leachate after the first 24 h period and the last 630 h of contact appeared to have little

further effect on transfer. The authors suggested that there are two potential mechanisms responsible for the observed transfer rates; 1) dislodgement of ultra-fine particles of dust adhering to the surface of the plastic; or 2) abrasion occurring when the chipped e-waste material rubs against each other and against the walls of the columns during end-over-end contacting.

Concentrations of BFRs in European landfill leachates have only been reported for Sweden (Table 3). Öman and Junestedt (2008) analysed leachate collected from Swedish municipal landfills containing household waste, industrial waste, construction and demolition waste, as well as ash, slag, sludge, lime, sediment and excavation material. The age of the waste in the landfills varied from a few years to 50 years. Concentrations of ΣPBDEs ranged from 10.2 ng L^{-1} to 19,463 ng L^{-1}, with those of TBBP-A reaching up to 20 ng L^{-1}.

In North America, Oliaei et al., (2002) reported concentrations of PBDEs in leachate sampled from five landfill sites with different waste characteristics (three municipal, one industrial, and one demolition) in Minnesota, USA. Concentrations of ΣPBDE ranged from 29 to 248 ng L^{-1}. The demolition waste landfill had the highest total PBDE concentrations, suggesting that the fate of building material waste warrants serious consideration. BDE-209 was the dominant congener found in leachate, 60% to 98% of the total PBDE contamination (Oliaei et al., 2010). The second phase of this study reported total PBDE concentrations of 7.1 ng L^{-1} in leachate from a recently closed landfill in Minnesota, USA (Oliaei et al., 2010). At this site, BDE-47 was the dominant congener found in leachate followed by BDE-99 and BDE-209 respectively. Water sampled from groundwater monitoring wells at the same site contained total PBDE concentrations of 0.052 ng L^{-1} (sum of dissolved and particulate phases).

In Japan (Osako et al., 2004), leachate samples were taken from seven different landfill sites and concentrations of PBDEs and TBBP-A determined. The study found substantial differences in the concentrations of BFRs in the raw leachate of each landfill site, with PBDE concentrations expressed as the sum of BDE-47, BDE-99 and BDE-100 ranging from <0.008 to 4 ng L^{-1}. In particular, leachate from one section on a

site that contained both crushed fragments of bulk wastes such as WEEE, as well as sewage sludge containing a “large amount” of organic matter; showed an extremely high concentration of PBDEs (e.g. 3.2 ng L^{-1} tetra-BDE, 1.8 ng L^{-1} penta-BDE, and 11 ng L^{-1} hepta-BDE). TBBP-A concentrations recorded in this study ranged from <1 to 620 ng L^{-1}, and it was even found in treated leachate at <1 to 11 ng L^{-1}. Furthermore, relatively high correlation coefficients were observed between concentrations of each PBDE homologue group and chemical oxygen demand (COD) (R = 0.73, 0.90 and 0.92 for tri-, tetra- and penta- BDE homologues respectively) and UV260 (R = 0.80, 0.93 and 0.93 for tri-, tetra- and penta- BDE homologues respectively), both important indicators for DHM. The authors stated that DHM has the potential to enhance leachability of hydrophobic organic pollutants (HOPs) by complex interactions. The presence of DHM was shown to significantly raise the leachability of HOPs, once DHM concentrations exceed a critical micelle concentration. Hydrophobic single tail regions are sequestered to the centre of the micelles leaving the hydrophilic head regions in contact with the surrounding solvent. However, the study found no correlation between concentrations of TBBP-A and either UV260 or COD. The authors hypothesised that more hydrophobic HOPs have greater affinity to DHM and suggested that the relatively higher hydrophobicity of PBDEs relative to TBBP-A, may account for the observed enhanced leachability of PBDEs over TBBP-A. Osako et al., (2004) also suggested that this may be one reason why TBBP-A does not correlate with UV260 and COD. However, as Table 1 shows, the water solubility of TBBP-A is very similar to that of the lower PBDE homologues which did correlate with COD and UV260, and other factors are thus likely involved.

Choi et al. (2009) conducted leaching tests for PBDEs, polybrominated biphenyls, polybrominated phenols and TBBP-A in plastic samples in the presence of DHM. Their results clearly show that BFRs can be leached by organic matter. While their experiments provide a valuable illustration of the importance of DHM in enhancing the leachability of BFRs, the authors also highlight that conditions within MSW landfills are more complicated, given the high organic matter loadings in leachate and complex interactions between a wide range of heterogeneous BFR waste, non-FR waste, sludge, etc..

Some plausible reasons why DHM has the ability to decrease pollutant/solid-phase interaction include: solubilisation, hydrolysis, catalysis, and photosensitisation mechanisms (Choi et al., 2009). Although it is logical to assume that only the BFRs distributed along the surface of a polymer can be leached by a solvent, other chemical engineering studies have reported sorption, diffusion, and permeation in the polymer matrix (Harogoppad and Aminabhavi, 1991; Gamst et al., 2003; Hansen, 2004; cited in Choi et al., 2009). Such interactions will likely involve multiple processes and vary in accordance with a variety of parameters such as temperature, solvent, and the molecular weight and morphology of the polymer (Choi et al., 2009).

Odusanya et al., (2009) reported concentrations of PBDEs in leachate collected from five landfill sites in South Africa. Expressed as the sum of BDEs-28, -47, -66, -71, -75, -77, -85, -99, -100, -119, -153, -154 and -183, concentrations ranged from 8.4 to 54.8 ng ΣPBDEs L^{-1} across the five sites. The dominant congeners found in the leachate were BDEs-28, -47, -71 and -75. The site with the highest concentrations of PBDEs also had the highest COD value, further supporting the influence of DHM on leaching. More recently Daso et al., (2013) reported PBDE concentrations from leachate at three landfill sites in Cape Town, South Africa. Leachate was collected on six occasions at bi-monthly intervals. Concentrations of the sum of BDEs-28, -47, -99, -100, -153, -154, -183 and -209 ranged from 45 to 17,953 ng ΣPBDEs L^{-1}, 2.25 to 164 ng ΣPBDEs L^{-1} and 13.3 to 9,360 ng ΣPBDEs L^{-1} for the three landfills.

PBDEs were detected in leachate from 26 out of 28 landfill and dumpsites across Canada (Li et al., 2012). While 59 PBDE congeners were monitored in all samples, only BDEs-47, -99, -100, -153, -154, -183, -206, -207, and -209 were detected frequently. The sum of these 9 congeners constituted more than 99% of the total PBDEs measured. Concentrations ranged substantially from 0.03 to 1,020 ng ΣPBDEs L^{-1}, with an average of 166 ng ΣPBDEs L^{-1}. The dominant congener was BDE-209 with a mean contribution of 52%.

Recently, Zhou et al., (2013) reported BFR concentrations from raw (ΣPBDEs 5.67 ng L^{-1}; TBBP-A 15.4 ng L^{-1}) and treated (ΣPBDEs <6.1 ng L^{-1}; TBBP-A <4.5 ng L^{-1}) landfill leachates from Laogang landfill site, Shanghai, China. Elsewhere in Asia, Kwan et al., (2013) reported PBDEs in leachate from ten MSW dumping sites located within eight tropical countries viz: Laos, Cambodia, Vietnam, India, Indonesia, Thailand, the Philippines, and Malaysia. Concentrations ranged from 3.7 to 133,000 ng ΣPBDEs L^{-1}. Debromination of PBDE technical mixtures (including BDE-209) is implied by the presence in leachate of congeners that are either absent from or present only in trace concentrations in commercial formulations (e.g., BDEs-208, -207, -206, -202, -188, -179, -49, -17/25, -8, and -1). Further discussion of such debromination follows in section 2.3.

2.3 Debromination and degradation

There is strong evidence that BDE-209 debrominates over time, forming lower brominated PBDEs with stronger bioaccumulation characteristics and higher toxicity (Danon-Schaffer, 2010; Kajiwara et al., 2008, 2013; Schenker et al., 2008; Stapleton and Dodder, 2008). Little information is available in the literature on the degradation pathways/kinetics of PBDEs. Work by Danon-Schaffer and Mahecha-Botero (2010) details a simplified degradation/debromination pathway based on stepwise debromination of each homologue group of congeners to the next (lower) one, beginning with BDE-209 and extending ultimately to low molecular weight congeners (tri-BDEs, di-BDEs and mono-BDEs). PBDE congeners lose bromines due to reductive debromination, photolysis, and microbial degradation in anaerobic environments (Danon-Schaffer and Mahecha-Botero, 2010). Reported BDE-209 photodegradation half-lives range between <15 minutes up to 408 days, depending on the matrix with which it is associated and the radiation wavelengths (Stapleton, 2008). It is unclear to what extent degradation occurs in the natural environment as shielding effects likely limit the amount of UV light to which the PBDEs are exposed (Domínguez et al., 2011). Also of concern, Kajiwara et al. (2013) showed that exposure to natural sunlight of textiles treated with Deca-BDE, resulted in the formation of polybrominated dibenzofurans (PBDFs) as products of photodecomposition. A maximum total PBDF concentration of 27,000 ng g^{-1} was reached after 329 days of exposure. This was

approximately 10 times the initial concentration. The authors also reported that di- to hexa-BDF congener concentrations increased continuously throughout the study. Interestingly, textiles that contained approximately 4% HBCD by weight showed no substantial loss of any HBCD diastereomers during the entire exposure period (371 days). This suggested that debromination and isomerisation of HBCD diastereomers did not occur and that HBCD is resistant to sunlight. However, this contrasts with the work of Harrad et al., (2009a) in which dust samples were exposed to light indoors for different periods of time with a control sample kept in darkness. Within the first week of exposure there was a significant shift from γ-HBCD to α-HBCD and evidence of HBCD degradation in the presence of light. The experimental data suggested a rapid photolytically mediated shift in the diastereomer profile and a slower degradative loss of HBCDs via elimination of HBr to degradation products pentabromocyclododecenes (PBCDs) and tetrabromocyclododecadienes (TBCDs). The difference between the two studies may be an indication of the influence of the material with which the HBCD is associated.

Analysis of dust samples from inside TV casings detected elevated concentrations of PBDEs. In one television studied, lower brominated homologues displayed elevated concentrations in dust relative to those in the plastic components (Takigami et al., 2008). While one explanation for this is that lower congeners transfer more efficiently via volatilisation and subsequent deposition to dust, another suggestion proposed by the authors was that the PBDEs detected in the dust might be transformed (e.g., through debromination and oxidation) during the transfer from components to dust. In a similar vein, Harrad et al., (2009a) reported that dust collected from within the casing of a HBCD flame retarded TV showed a substantially higher ratio of γ-HBCD to α-HBCD than dust sampled at increasing distances from the source. This is consistent with a photolytically mediated shift in the diastereomer profile. Chen et al., (2010) reported elevated ratios of BDE-208:BDE-183 and BDE-208:BDE-209 in TV/PC display casings, and PC components sampled in South China. The authors attributed these ratios to the decomposition of higher brominated PBDEs during the process of manufacturing, use and/or recycling of PBDE-containing products, in addition to degradation in the environment. Elevated values of such ratios were also reported by Muenhor et al.,

(2010) in dust samples taken from e-waste storage facilities in Thailand. The authors suggest that debromination of BDE-209 to BDE-208 had taken place during the lifetime of the e-waste and further hypothesised that the elevated abundances of BDE-208 and of the other nona-BDEs (BDE-206 and BDE-207) found in their dust samples arose largely as a result of direct migration of such congeners from stored e-waste.

Finally, reductive debromination of deca- , nona- and octa-BDEs, to lower brominated congeners can occur in anaerobic environments (akin to landfill conditions) *via* microbial activity (Gerecke et al., 2005; He et al., 2006; Robrock et al., 2008). Gerecke et al., (2006) found that TBBP-A and HBCD also underwent microbially mediated degradation under anaerobic conditions in digested sewage sludge, with the half-life of α-HBCD almost twice that of β-HBCD and γ-HBCD. Additionally, it has been reported that BDE-209 and nona-BDEs can be debrominated by anaerobic sediment microbes (Parsons et al., 2004; Tokarz et al., 2008).

In summary, the available evidence suggests that the BFR content of landfilled waste will likely change over time, as a result of a variety of degradation processes.

2.4 Abrasion and weathering

Hale et al. (2002) conducted weathering experiments on BFR-treated PUF for several weeks under full sunlight conditions in summer. Typical daytime temperatures were as high as 30-35 °C and humidity generally exceeded 80%. Disintegration of the surface of the PUF occurred within four weeks and resulted in small, low-density fragments easily dispersed by precipitation or wind. Moreover, weathered PUF fragments appeared to preserve the original constituent pattern of Penta-BDE.

Work by Webster et al. (2009) using environmental forensic microscopy, suggests that physical abrasion is a viable mechanism via which BDE-209 can migrate from consumer products to indoor dust. BDE-209 has a very low vapour pressure, therefore the authors hypothesised that abrasion is a more plausible transfer mechanism than volatilisation – particularly in dust samples containing highly elevated concentrations of BDE-209. This was supported by the heterogeneous distribution of the bromine in

the dust samples. Furthermore, bromine-rich particles were not observed free in the dust but appeared to be embedded in a polymeric/organic matrix and associated with calcium. Calcium carbonate is a very common additive in plastics. This evidence supports the abrasion hypothesis in that BDE-209 is primarily present in dust samples containing highly elevated concentrations of this congener as inclusions in plastic particles. Given the conditions prevalent in landfills, it is not unreasonable to hypothesise that similar abrasive mechanisms will be at work on landfilled waste and thereby facilitate BFR emissions.

3. Analysis and discussion

Currently there appear little or no data on emissions of BFRs from waste soft furnishings in the literature. Indeed only a few data exist concerning the emissions of BFRs from landfill sites or during the incineration of MSW; as well as the potential for emissions during transport of waste to landfills or incinerators. The absence of data on these aspects constitute major research gaps. Fig. 1 illustrates the various potential pathways via which BFRs may migrate from waste during transport to and storage at waste treatment facilities as well as during the treatment process itself. The bulk of research into BFR emissions from waste focuses on primitive e-waste dismantling and recycling conducted in areas such as Taizhou, Zhejiang province and Guiyu, Guangdong province in China (Chen et al., 2008; Chen et al., 2009; Han et al., 2009) and is therefore not immediately relevant to disposal of waste soft furnishings under controlled conditions.

A small number of emission chamber experiments have shown that volatilisation of BFRs from a range of products including soft furnishings are amplified significantly at temperatures above 80 °C (Kajiwara and Takigami, 2013; Kemmlein et al., 2003). However, despite evidence that temperatures within landfills can reach up to 80-90 ˚C; to the authors' knowledge there have been no experiments conducted that examine the effect of temperature on the leachability of BFRs from waste.

As well as volatilisation and leaching, an additional migration pathway from waste of BFRs such as BDE-183 and BDE-209, is via fugitive emissions of dust to air by abrasion

during waste unloading and/or compacting by on site vehicles. However, there appear no studies to date that have measured the extent to which this occurs. Likewise, there exist no studies to date that examine the potential for fugitive (largely, but not exclusively particle-bound) emissions of BFRs as a result of the landfilling of residual bottom and fly ash generated by waste incineration.

As well as limited data on the extent and pathways of BFR emissions during waste treatment, our understanding of the factors influencing such emissions is hampered by our limited knowledge of environmentally-relevant physicochemical properties of some BFRs, e.g., aqueous solubility, and partition coefficients like K_{OW}, K_{OC}, and Henry's constant. While such physicochemical properties for lower brominated PBDEs are relatively well-characterised, those of BDE-209, TBBP-A, HBCD, and "novel" BFRs like decabromodiphenyl ethane (DBDPE) are subject to greater uncertainty. Enhanced understanding of these properties – and of factors like climate - is needed to facilitate understanding of how BFRs are leached from waste materials in a landfill setting. For example, while Odusanya et al (2009) reported higher concentrations of PBDEs in landfill leachate in winter compared to summer; it still appears likely that hotter climates will enhance the leachability of BFRs in landfill. As a result, compared to much of North America and northern Europe; subtropical and tropical regions such as southern China, Laos, Cambodia, Vietnam, India, Indonesia, Thailand, the Philippines, and Malaysia are unlikely to display similar BFR concentrations in landfill leachate.

Further international variability in BFR concentrations in landfill leachate will likely arise due to different waste management practices. For example, the low concentrations detected in leachate from Japanese landfills may well be attributable to the fact that 80% of MSW is incinerated in Japan. Hence, the proportion of Japanese landfill that is incinerator ash is high, and direct extrapolation of Japanese landfill leachate data to countries such as the UK where incineration is far less prevalent and BFR-containing waste is more likely landfilled untreated, appears unwise.

Given that in many (though not all) studies, BDE-209 is the dominant PBDE congener found in landfill leachates, this suggests that water solubility alone is not the primary

factor driving BFR leaching from landfilled waste. Understanding what does drive BFR leaching is important; while there are no reported measurements of HBCD concentrations in landfill leachates, the evidence for PBDEs suggests that leaching could constitute an appreciable pathway via which HBCD and related BFRs migrate into the environment. Specifically, Li et al., (2012) estimated average annual emissions from a single urban landfill in Canada to be 3.5 tonnes ΣPBDEs /year.

Moreover, evidence for reductive debromination of BFRs by microbes under anaerobic conditions suggests this could also occur in landfill, resulting in some instances in more toxic and bioavailable compounds, particularly during phase 2 and 3 of landfill leachate generation (Parsons et al., 2004; Gerecke et al., 2005, 2006; He et al., 2006; Robrock et al., 2008; Tokarz et al., 2008). While this hypothesis has yet to be verified fully; it is supported by the relatively higher abundances in landfill leachate of PBDE congeners that are absent from the commercial formulations (Kwan et al., 2013).

4. Conclusions

There has been very little research into the extent of emissions of BFRs from waste soft furnishings. The mechanisms via which BFRs migrate from such waste materials remain far from completely understood, and current understanding is almost entirely based on the larger – but still far from complete – database on emissions from WEEE and in-use materials. While – in addition to the burgeoning database on BFR emissions resulting from informal e-waste recycling activities - evidence exists of elevated airborne concentrations of HBCDs in the vicinity of a UK e-waste treatment facility together with the presence of BFRs (specifically PBDEs and TBBP-A) in landfill leachate; other studies of BFR emissions from regulated waste treatment activities remain few. Although BFRs are hydrophobic, evidence exists that their leachability from waste materials is substantially enhanced when DHM is present in the leachate. There is a need to enhance understanding of the factors influencing emissions and of the potential for BFR degradation under landfill conditions. Landfill sites already constitute an enormous reservoir of BFR-containing materials and commercial goods e.g. e-waste, building materials, carpets, furniture and upholstery fabrics. As a result, without careful management, such landfills will continue to act as substantial sources of BFRs

to the global environment, and the wisdom of continued landfilling of BFR-containing waste is questionable. For instance, Weber et al. (2011) suggest that such products should be destroyed or managed in an environmentally sound manner before they enter the waste stream, and that such BFR waste should not be landfilled or recycled in view of its toxicity and associated environmental concerns. While hitherto, scientific and societal focus has been on e-waste, this review highlights that many of the same concerns exist regarding emissions from waste soft furnishings, and that studies to enhance our currently scant understanding of BFR emissions from this important waste stream constitute an urgent research priority.

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Table 1: Selected physicochemical properties of brominated flame retardants

Compound	Log K_{OW}	Aqueous Solubility (mg/L)	Log K_{OA}	Vapour Pressure
BDE-15	5.48 [a]	0.821 [b]	8.72 [g]	8.80×10^{-3} [i]
BDE-28	5.80 [a]	0.421 [b]	9.50 [h]	1.57×10^{-3} [i]
BDE-47	6.39 [a]	0.112 [b]	10.53 [h]	2.50×10^{-4} [i]
BDE-85	7.37 [b]	0.097 [b]	11.69 [b]	9.86×10^{-6} [j]
BDE-99	6.76 [a]	0.077 [b]	11.31 [h]	5.00×10^{-5} [i]
BDE-100	6.53 [a]	0.085 [b]	11.13 [h]	2.86×10^{-5} [j]
BDE-153	7.08 [a]	0.031 [b]	11.82 [h]	5.80×10^{-6} [i]
BDE-183	8.27 [b]	-	11.96 [h]	4.68×10^{-7} [j]
BDE-209	9.97 [b]	0.002 [b]	15.73 [b]	1.43×10^{-8} [b]
HBCD	5.60 [c]	0.030 [e]	10.46 [e]	6.27×10^{-5} [k]
TBBP-A	5.90 [d]	0.099 [f]		4.72×10^{-9} [f]

[a] Wania & Dugani (2003)
[b] Yue & Li (2013)
[c] MacGregor & Nixon (1997)
[d] MacGregor & Nixon (2001)
[e] Marvin et al., (2011)
[f] Kuramochi et al., (2008)
[g] Li et al., (2006)
[h] Harner & Shoeib (2002)
[i] Wong et al., (2001)
[j] Tittlemier et al., (2002)
[k] USEPA (2008)
Nb : estimated values used where not measured

Table 2: Concentrations of brominated flame retardants in ambient air in the vicinity of waste treatment facilities

Compound	Phase	Method of waste disposal	Concentrations (ng m^{-3})	Country
ΣHBCDs	Both (total)	WEEE recycling	22	UK [a]
Σ_{24}PBDEs	Particulate only	WEEE recycling	175.79 – 233.16	Sweden [b]
Σ_{10}PBDEs	Vapour only	WEEE storage	0.008 – 0.15	Thailand
BDE-183	Particulate only	Active landfill	0.001 – 0.011	Germany
BDE-183	Particulate only	Closed landfill	0.001 – 0.003	Germany
ΣPBDEs	Both (total)	Active landfill	0.00108 – 0.1519	Canada [e]
ΣPBDEs	Both (total)	Closed landfill	17.3	USA [f]
ΣPBDEs	Both (total)	Incineration plant	2	Canada [g]
Σ_7PBDEs	Both (total)	Incineration plant	0.00224 – 0.02132	Sweden [h]

[a] Harrad et al., (2010)
[b] Julander et al., (2005)
[c] Muenhor et al., (2010)
[d] Weinberg et al., (2011)
[e] St-Amand et al., (2008)
[f] Oliaei et al., (2010)
[g] Alaee, (2001)
[h] Agrell et al., (2004)

Table 3: Concentrations of brominated flame retardants in landfill leachate and related aqueous samples

Compound	Aqueous medium	Site Category	Concentration (ng L^{-1})	Country
ΣPBDEs	Raw Leachate	Active landfill	10.2 – 19,463	Sweden [a]
TBBP-A	Raw Leachate	Active landfill	<1 – 20	Sweden [a]
ΣPBDEs	Raw Leachate	Active landfill	29 – 248	USA [b]
ΣPBDEs	Raw Leachate	Closed landfill	7.1	USA [c]
ΣPBDEs	Groundwater	Closed landfill	0.052	USA [c]
Σ_3PBDEs	Raw Leachate	Active landfill	<0.008 – 4	Japan [d]
TBBP-A	Raw Leachate	Active landfill	<1 – 620	Japan [d]
TBBP-A	Treated Leachate	Active landfill	<1 – 11	Japan [d]
Σ_{13}PBDEs	Raw Leachate	Active landfill	8.392 – 54.761	S. Africa [e]
Σ_8PBDEs	Raw Leachate	Active landfill	2.25 – 17,953	S. Africa [f]
Σ_{59}PBDEs	Raw Leachate	Active landfill	0.03 – 1,020	Canada [g]
Σ_{30}PBDEs	Raw Leachate	Active landfill	5.67	China [h]
Σ_{22}PBDEs	Treated Leachate	Active landfill	<6.10	China [h]
TBBP-A	Raw Leachate	Active landfill	15.41	China [h]
TBBP-A	Treated Leachate	Active landfill	<4.50	China [h]
Σ_{46}PBDEs	Raw Leachate	Active waste dump	3.7 – 133,000	S.E. Asia [i]

[a] Öman and Junestedt, (2008)
[b] Oliaei et al., (2002)
[c] Oliaei et al., (2010)
[d] Osako et al., (2004)
[e] Odusanya et al., (2009)
[f] Daso et al., (2013)
[g] Li et al., (2012)
[h] Zhou et al., (2013)
[i] Kwan et al., (2013)

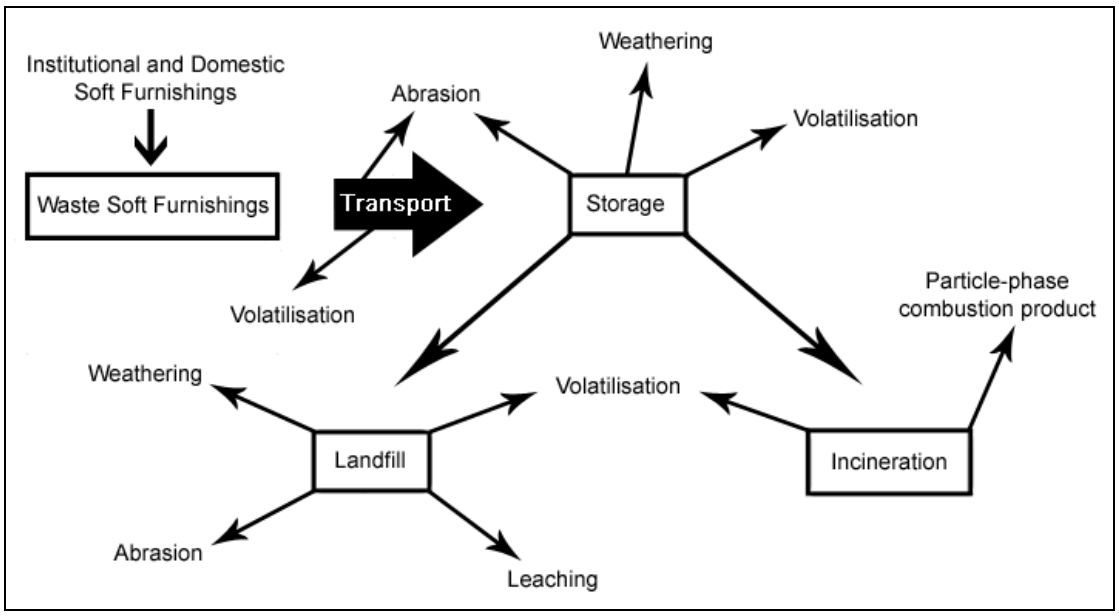

Figure 1: Potential BFR migration pathways from waste soft furnishings